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(54) **Method of oxidatively degrading an olefinic polymer to produce an oxidised polymer product useful as a viscosity index improvement agent for a lubricating oil.**

(57) A method of oxidatively degrading an olefinic polymer comprises oxidising the olefinic polymer in an inert solvent in the absence of molecular oxygen and in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised polymer product is obtained. The oxidised polymers produced by this method can be further reacted with a nitrogen-containing compound such as a polyalkylene polyamine. The oxidised polymer products are of value as viscosity index improvement agents when incorporated in lubricating oil compositions.

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Method of oxidatively degrading an olefinic polymer to produce an oxidised polymer product useful as a viscosity index improvement agent for a lubricating oil

This invention relates to a method of oxidatively degrading an olefinic polymer and to the use of the oxidised polymer so-produced as a viscosity index improvement agent in a lubricating oil composition.

An important property of a lubricant composition is the rate at which its viscosity changes as a function of temperature. The relationship between the viscosity and temperature is commonly expressed in terms of the viscosity index (V.I.). Lubricant compositions which change little in viscosity with variations in temperature have greater viscosity index than do compositions whose viscosity is materially affected by changes in temperature. It is readily apparent, therefore, that one of the major requirements of lubricating oils or other hydrocarbon oil products is their satisfactory viscosity-temperature characteristics. These characteristics are necessary in order that the viscosity of the oil will not become too low but will show an equally good performance within a relatively wide temperature range to which it may be exposed in service. The wider the possible temperature variations, the smaller should be the change in viscosity with temperature. Hence, the viscosity-temperature characteristics of a lubricant which is used in applications where wide variations in temperature are encountered are of great importance and lubricant compositions having high viscosity indices are highly desirable.

A variety of polymeric or high molecular weight materials have been described as viscosity index improvers for lubricants and have been prepared via an air or oxygen sparging oxidation process which involves the use of molecular oxygen in at least one step in the preparation thereof. For example: U.S. Patent No.

3,417,020 teaches lubricating oil compositions of improved viscosities containing degraded ethylene-alpha-olefin polymers wherein the degraded polymers have been hydroxylated. The hydroxylated degraded polymers are prepared by hydroperoxidizing the polymer with subsequent reduction of the hydroperoxide groups to yield degraded products containing hydroxyl groups and minor amounts of carboxyl, keto and aldehyde groups.

U.S. Patent No. 3,756,954 teaches the preparation of viscosity index improvers prepared by air oxidation of interpolymers of ethylene and propylene in the presence of an aliphatic amine.

British Patent Application No. 2,040,296A teaches the preparation of a viscosity index improver additive by oxidatively and mechanically degrading an ethylene copolymer containing as one of its components from 0.05 to 3% of 2,5-norbornadiene.

U.S. Patent No. 3,316,177 teaches reaction of polyamine with the reaction product of maleic anhydride with an oxidized interpolymer of ethylene and propylene, as a sludge dispersant in lubricant and fuel compositions.

U.S. Patent No. 3,404,091 describes the preparation of nitrogen containing polymers, useful as sludge dispersants and viscosity index improvers, by grafting polar monomers such as acrylonitrile on to hydroperoxidized ethylene-propylene copolymers.

U.S. Patent No. 3,687,849 describes the preparation of viscosity index improvers, pour point depressants and dispersants, for fuels and lubricants, by grafting various unsaturated monomers on to a degraded, oxidized, interpolymer of ethylene and propylene.

U.S. Patent No. 3,687,905 describes the preparation of additives for fuels and lubricants by the reaction of an unsaturated acid, such as maleic acid or anhydride, with an oxidized, degraded interpolymer of ethylene and propylene, followed by reaction with a

polyamine.

U.S. Patent No. 3,769,216 discloses the preparation of lube oil additives by the condensation of an amine with an oxidized ethylene-propylene copolymer, prepared by air blowing in the presence of a peroxide (also see U.S. Patent 3,785,980), or by mastication of the polymer in the presence of oxygen.

While not related to the preparation of viscosity index improvers, other oxygen-sparging oxidation methods applied to olefinic polymers are described in the prior art, for example, in U.S. Patent Nos. 3,153,025, 3,110,708 and 3,232,917.

With respect to these prior art methods, there is considerable concern about the safety aspects such as the possibility of an explosion using air oxidation of an olefinic polymer solution involving relatively large quantities of molecular oxygen and a large volume of hydrocarbon.

It has now been found in accordance with the invention that the oxidation of olefinic polymers is advantageously carried out in solution using a mixture of organic peroxide and hydroperoxide as the oxidizing agent. This system is preferred because it forms a single-reaction phase with the polymer solution, it is relatively non-corrosive, and it does not have the hazards associated with the air oxidation of hydrocarbons.

Thus in accordance with one aspect of the invention, there is provided a method of oxidatively degrading an olefinic polymer in the absence of molecular oxygen, which comprises oxidizing the olefinic polymer in an inert solvent in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised

polymer product is obtained.

The oxidized polymer obtained by the foregoing method may be further reacted with one or more functional group-containing compounds, such as non-tertiary nitrogen-containing compounds. Both the oxidized polymer and the functionalized derivatives thereof are viscosity-index improvement agents for lubricating oils. The polymers so produced also show excellent dispersancy properties in lubricatinbg oils and have excellent thickening power and shear stability.

The term "olefinic polymer" is used herein to mean polymers derived from olefinically unsaturated hydrocarbon monomers. The polymer may be a homopolymer, a copolymer, which term includes random, and block copolymers, or a terpolymer or tetrapolymer, etc. Suitable homopolymers include polybutenes, such as polyisobutene having an $\overline{M}_n$ in the range 5,000 to 60,000, preferably in the range 10,000 to 45,000. Suitable copolymers include ethylene copolymers, especially copolymers of ethylene and a C_3-C_8 alpha-olefin such as ethylene/propylene, e.g. ethylene/propylene copolymers containing from 20 to 65, preferably from 35 to 45 mole percent propylene and having an $\overline{M}_n$ in the range 10,000 to 200,000, preferably from 20,000 to 70,000, and copolymers of a vinyl aromatic monomer, e.g. styrene, alphamethyl styrene or vinyl naphthalene, and a conjugated diene monomer, e.g. butadiene or isoprene, of which hydrogenated block copolymers containing from 10 to 40, preferably from 15 to 35 weight percent of the vinyl aromatic monomer and having an $\overline{M}_n$ in the range 25,000 to 125,000, preferably from 50,000 to 125,000, are preferred. Such polymers are described in, for example, U.S. Patents Nos. 3,994,815; 3,775,329; 3,668,125 and 3,763,044. Suitable random copolymers are described in for example, U.S. Patents Nos. 3,554,911; 3,630,905; 3,752,767 and 3,772,169. Suitable terpolymers include terpolymers of ethylene, a C_3 to C_8 straight- or branched-

chain alpha-olefin, e.g. propylene, and a non-conjugated acyclic or alicyclic diolefin, e.g. 1,4-hexadiene, 1,5-heptadiene, 1,6-octadiene, 1,4-cyclohexadiene, 5-methylene-2-norbornene or 5-ethylidene-2-norbornene, generally containing from 30 to 85, preferably from 40 to 70 mole percent ethylene, from 15 to 70, preferably from 30 to 60 mole percent alpha-olefin and from 0.5 to 20 mole percent, preferably from 1 to 15, even more preferably from 2 to 10 mole percent diene and having an $\bar{M}_n$ in the range from 15,000 to 200,000, preferably from 20,000 to about 70,000. Preferred terpolymers are terpolymers of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene. Suitable tetrapolymers include tetrapolymers of ethylene, a C_3 to C_8 straight- or branched-chain alpha-olefin and two non-conjugated acyclic or alicyclic diolefins. The preparation of the terpolymers, using Ziegler-Natta catalysts, is described, for example, in U.S. Patents Nos. 2,933,489, 3,000,866 and 3,093,621. These terpolymers and tetrapolymers, which are primarily produced for use in elastomeric compositions, are characterized by the absence of chain or backbone unsaturation and contain sites of unsaturation in groups which are pendant to or in cyclic structures outside of the main polymer chain. It is an advantage of the present invention that oxidation occurs substantially on the main backbone chains of the polymers in preference to the groups pendant to or outside the backbone chain.

Mixtures of polymers may also be used, if so desired, in the process of the invention. Thus blends may be formulated to provide desirable properties, e.g. improved low temperature thickening. Suitable mixtures of polymers include mixtures of two or more ethylene/propylene copolymers having different ethylene-propylene ratios and/or molecular weights and mixtures of an ethylene/propylene copolymer and a polyisobutene.

In accordance with the present invention, the

aforementioned olefinic polymers are employed as starting materials in a controlled oxidation reaction using a mixture of at least one peroxide and at least one hydroperoxide referred to hereinabove as the oxidant mixture. More specifically, the oxidized olefinic polymers resulting from this invention are prepared by dissolving the olefinic polymer in an inert solvent at a temperature generally in the range of from 60°C to 250°C, using agitation. A mixture of radical initiators is added to the reaction medium under a pressure of from 0 to 1,000 psig (1 to 70.3 kg/sq.cm) and the reaction is continued for a period of from about 0.05 to 20 hours. There is essentially no introduction of oxygen from a separate source into the reaction medium during the oxidation reaction.

The final polymeric product may be recovered from solution by evaporation of the solvent or by precipitation with a non-solvent or by any other suitable method. Alternatively, prior to removal of the inert solvent, a lubricating oil may be added directly to the reaction mixture and the inert solvent removed by vacuum distillation.

The oxidized olefinic polymer can be made in batch or continuous operation. In batch operation, the individual components are added to a suitable reaction vessel together or in discrete portions and dissolved in an inert solvent. In continuous operation the reactant or reactants are added continuously to a horizontal or vertical reaction zone at appropriate feed rates in a diluent or neat at temperatures to promote easy handling, reaction and solubility.

The compositions of this invention have a thickening power in the range of from 10-35 cSt. "Thickening power" as used herein is defined as the viscosity at 100°C of a neutral oil having a viscosity at 40°C of 28.6 cSt and at 100°C of 4.7 cSt, containing 2.8 weight percent of the dry polymeric composition. Thickening power is thus measured as an actual viscosity of the oil

due to incorporation of the polymer. Thickening power is directly related to the molecular weight of the polymer, but is used instead of molecular weight because of the ease of measurement and greater practical significance of data. While the thickening power of the compositions of this invention may be broadly defined as being in the range of 10-35 cSt, thickening power is more usually in the range of 15-25 cSt.

The oxidation is carried out in the presence of a mixture of at least one peroxide and at least one hydroperoxide in a mole ratio of peroxide to hydroperoxide in the range from 3.2:1 to 0.4:1 and preferably in the range from 1.7:1 to 0.8:1. Surprisingly, it has been found that use of the combination is much more efficient in oxidizing and degrading the olefinic polymer than the use of either the peroxide or hydroperoxide alone.

Representative of the peroxides which may be used in the mixture are, for example, cumene peroxide, dicumyl peroxide, benzoyl peroxide, dilauryl peroxide, di(n-propyl)peroxydicarbonate, tertiary butylperoxyisobutyrate, 2,5-dimethyl-2,5-di(t-butylperoxy) hexane and acetyl cyclohexylsulfonyl peroxide. Representative of the hydroperoxides which may be used are, for example, cumene hydroperoxide, hydrogen peroxide, tertiary butyl hydroperoxide and 2,5-dihydroperoxy-2,5-dimethylhexane. It is also possible to use a single compound which contains at least one peroxide group and at least one hydroperoxy group, or a mixture of such compounds. The concentration of the oxidant mixture relative to the olefinic polymer in solution is generally in the range from 1 to 20% by weight, preferably from 2 to 15 percent and most preferably from 5 to 12% by weight.

The oxidation is carried out in a solvent substantially inert to the reaction conditions. Solvents such as toluene, xylene, hexane, or mineral neutral oils can be used. Preferred solvents are benzene, chlorobenzene and t-butylbenzene. The solvent may suitably be present in an amount in the range from 20 to 99%,

preferably from 50 to 95%, and more preferably from 70 to 90% by weight, based on the weight of the olefinic polymer.

The oxidised polymer product obtained by the oxidation reaction is an oil-soluble product of lower molecular weight than the starting material. The molecular weight depends upon the extent and conditions employed during the oxidation reaction. Ultimately, the intermediate oxidized polymers are converted by oxidation reactions to fragmented or degraded polymer materials containing carbonyl groups. The more vigorous the oxidation conditions and the longer the length of time maintaining such conditions, the greater the number of carbonyl groups introduced into the starting material. It is sufficient, however, than on an average at least one carbonyl, preferably in the form of a carboxyl-carbonyl, is introduaced into each molecule of the starting material.

The oxidized polymer materials have a viscosity average molecular weight of from about one-half to one-tenth of the molecular weight of the original material. The product of the oxidation process will generally have from 0.01% to 1% by weight oxygen and preferably from 0.2% to 0.8% by weight oxygen.

In accordance with another aspect of the invention there is provided a lubricating oil composition comprising an oil of lubricating viscosity and, as a viscosity index improvement agent, an oxidized olefinic polymer product containing carbonyl groups obtained by the method of the invention as hereinbefore described. Preferably the polymer product is present in the lubricating oil in an amount of from 0.05 to 20% by weight.

It is believed that the majority of the carbonyl groups introduced into the polymer, or at least the ethylene/propylene copolymers, by the oxidative method of the present invention tend to be carboxylic acid carbonyl groups rather than aldehydrocarbonyl and ketocarbonyl

groups. Carboxylic acid carbonyl and ketocarbonyl groups are favoured for the further chemical conversion of the oxidized polymer. The oxidized olefinic polymers may be reacted through their carbonyl groups with a variety of other reagents, e.g., hydrogen or nitrogen, oxygen, sulfur, boron and/or phosphorus-containing compounds to form multifunctional products. It is preferred to react the oxidized olefinic polymers with one or more nitrogen-containing compounds (other than a tertiary nitrogen compound), such as ammonia and organic amines which may be mono, di or polyamines containing at least one primary or secondary amino group, and, advantageously polyalkylene polyamines having the general formula:

$$H_2N(CH_2.\underset{\displaystyle R^1}{\underset{|}{CH}}.NH)_xH \qquad (I)$$

wherein each R^1 is hydrogen or a C_1 to C_6 alkyl group, preferably hydrogen, and x is an integer in the range from 1 to 10, preferably in the range from 2 to 5, to form a nitrogen-containing product having both viscosity index improvement and dispersancy properties. Examples of suitable nitrogen-containing compounds include 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; diethylene triamine, triethylene tetramine, tetraethylene pentamine; 1,2-propylene diamine; di-(1,2-propylene) triamine, di-(1,3-propylene) triamine and N,N-di-(2-aminoethyl) ethylene diamine.

Other polyamine compounds that may be used include the N-aminoalkyl piperazines of the general formula:

$$NH_2-(CH_2)_n-N\begin{matrix} \diagup CH_2-CH_2 \diagdown \\ \diagdown CH_2-CH_2 \diagup \end{matrix}N-R$$

wherein n is from 1 to 3, and R is hydrogen or an

aminoalkyl radical containing from 1 to 3 carbon atoms. Specific examples include N-(2-aminoethyl) piperazine, N-(2-aminoisopropyl) piperazine and N,N'-di-(2-aminoethyl) piperazine.

The polyalkylene polyamines which may be used in the practice of this invention can be either pure alkylene amines or they can be commercial mixtures. For example, one process for preparing alkylene amines involves the reaction of an alkylene chloride such as ethylene chloride or propylene chloride with ammonia, which results in the production of somewhat complex mixtures of alkylene amines including various piperazines. One useful commercial product is a mixture of ethylene amines prepared by the reaction of ethylene chloride and ammonia and having a composition that corresponds to that of a tetraethylene pentamine. One such mixture is known in the trade under the name "Polyamine H".

Still other alkylene amino compounds that can be used include dialkylamino alkyl amines such as dimethylamino methyl amine, dimethylamino propyl amine, and methylpropylamino amyl amine. These may be characterized by the general formula:

$$H_2N-R_1-N\begin{matrix} \diagup R_2 \\ \diagdown R_3 \end{matrix}$$

wherein R_1 is an alkylene radical, e.g., an ethylene, propylene, or butylene radical, and R_2 and R_3 are C_1 to C_5 alkyl radicals.

Other useful amines include N,N-di-(2-hydroxyethyl)-1,3-propylene diamine; 3-dodecyloxypropylamine; N-dodecyl-1,3-propane diamine; tris-hydroxymethyl aminomethane, diisopropanolamine and diethanolamine. There may also be used the mono-succinimide, formed by reacting an alkenyl-succinic anhydride such as

polyisobutene succinic anhydride with either a diamine or a polyalkylene polyamine having the formula (I).

The reaction conditions for the reaction of carbonyl groups with nitrogen-containing compounds are well-known in the art. Thus, for example, the condensation of the oxidized rubbery polymers containing a plurality of carbonyl groups and preferably carboxylic acid carbonyl groups with a primary or secondary amine to an aminated carbonyl compound useful as a lubricating oil additive is carried out in the presence of a substantially inert solvent at a temperature generally of from 100°C to 280°C for a period of generally from 1 to 24 hours. Typical solvents include the hydrocarbon oil into which the product is designed to be incorporated. Alternatively, another solvent miscible in the lubricating oil and liquid at the reaction temperature may serve as the reaction medium. This would include aromatics such as mixed xylenes, as well as aliphatic oils and halogenated materials such as o-dichlorobenzene. The mole ratio of polyamine to oxidized polymer is generally in the range from 0.2 to 2.5 moles of amine per mole of oxidized polymer.

Methods for preparing aminated polyolefins are described for example in U.S. Patents Nos. 3,785,980; 4,132,661 and 4,317,772.

In a similar manner other preferred derivatives of the oxidized olefinic polymers which are useful as viscosity-index improvers may be formed by reaction with (1) reducing agents or hydrogen to form hydroxylated polymers are described in U.S. Patent No. 3,388,067, which hydroxylated polymers may be further reacted with isocyanates as described in U.S. Patent No. 3,404,092, (2) oxygen-containing compounds such as maleic anhydride followed by reaction with a polyamine as described in U.S. Patents Nos. 3,687,905 and 3,316,177 and (3) sulfur compounds or sulfur compounds and an amine as described in U.S. Patents Nos. 4,317,738 and 4,320,017.

It will be appreciated that the invention includes within its scope a lubricating oil composition comprising an oil of lubricating viscosity and, as a viscosity index improvement agent, a further-reacted and functionalized oxidized olefinic polymer product as described above. Preferably the polymer product is present in the lubricating oil in an amount of from 0.05% to 10% by weight.

The lubricating oils used in the compositions of the invention are oils of lubricating viscosity, and particularly of the type useful in internal combustion engines and can be predominantly paraffinic or naphthenic, or they can be a mixture of both types of mineral oils, as well as synthetic oils which include polymers of various olefins, generally of 10 carbon atoms or higher, and alkylated aromatic hydrocarbons. In general, the lubricating oil will preferably be a relatively highly refined mineral oil of predominantly a paraffinic nature and will have a viscosity in the range of from 2 to 20 cSt at 100°C.

Other additives, such as detergents, rust inhibitors, anti-oxidants, anti-wear agents, etc., may also be present in the lubricating oil composition. These other additives will be present in conventional concentrations. Preferred additives which may be present in the lubricating oil composition in effective amounts, and preferably in the concentration range of from 0.01% to 5%, include neutral and overbased alkali and alkaline earth metal sulfonates or phenates or combinations thereof, a metal dihydrocarbyl dithiophosphate such as a zinc dialkyl dithiophosphate and/or an alkenyl succinimide or succinate or mixtures thereof.

The invention is illustrated by the following non-limitative Examples.

Example 1

A pipe reactor consisting of 7.62 m of 12.7 mm carbon steel pipe heated by steam tracing was used for

this reaction. A solution containing 8% by weight of an ethylene/propylene/1,4-hexadiene terpolymer (a product manufactured by Du Pont Company, Wilmington, Delaware, USA and sold under the trade name Ortholeum 2038, which is a terpolymer having about 60 mole percent ethylene groups, 39 mole percent propylene groups and 1 mole percent 1,4-hexadiene groups and having a molecular weight of about 250,000) in chlorobenzene was first pumped through a hot oil heat exchanger and heated to a temperature of 167°C. The solution was then fed into the reactor at 340 g/min. The reactor was kept at 155°C using steam and the pressure was maintained at 200 psig (14 kg/sq.cm). At the front end of the reactor two other solutions were pumped in - a 50% by weight dicumyl peroxide in chlorobenzene at 2 ml/min. and an 8% by weight hydrogen peroxide in water at 8 ml/min. At the end of the reactor 100 Neutral oil was line mixed with the reaction mixture at 272.4 g/min.

50 gallons (0.189 m^3) of the reaction mixture containing oil was stripped in a 100 gallon (0.379 m^3) glass kettle at 300°F (148.9°C) and 20 mm Hg for 1 hour. Then, it was transferred to a 50 gallon (0.189 m^3) stainless stell kettle and stripped at 400°F (204.4°C) and 20 mm Hg for 1 hour.

The final product has the following properties:

Viscosity at 100°C (9.75% polymer product by weight)= 281.6 cSt

Viscosity of 2.8% solution in 100 N oil = 17.0 cSt (Thickening Power)

Example 2

The product of Example 1 was line mixed with a 3.7% solution of ethylene diamine (EDA) in C_{7-9} aromatic hydrocarbon solvent mixture. The polymer solution was pumped at 133.5 ml/min. and the EDA solution was pumped at 33.4 ml/min. The total mixture was then fed into a wiped film evaporator kept at 450°F (232.2°C). The stripped product was filtered through a 100 μ filter and

had the following properties:

Flash Point = 390°F (198.9°C)

Viscosity at 100°C (9.75% by weight product) = 426.4 cSt

Viscosity of 2.8% solution in 100 N oil = 20.7 cSt (at 100°C)

Nitrogen content = 149 ppm.

Multi-grade lubricating oils with good dispersancy and shear stability were prepared using the product of this Example.

Example 3

A pipe reactor consisting of 7.62 m of 12.7 mm carbon steel pipe heated by steam tracing was used for this reaction. A solution containing 8% by weight of the ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 in chlorobenzene was first pumped through a hot oil heat exchanger and heated to a temperature of 216°C. The solution was then fed into the reactor at 0.8 lb/min. (0.36 kg/min). The reactor was kept at 188°C using steam and the pressure was maintained at 200 psig (14.06 kg/cm^2). At the front end of the reactor two other solutions were pumped in - a 6.25% by weight dicumyl peroxide in chlorobenzene at 2 ml/min. and a 25% by weight cumene hydroperoxide in chlorobenzene at 9.2 ml/min. At the end of the reactor 100 Neutral oil was line mixed with the reaction mixture at 0.36 lbs/min (0.16 kg/min).

50 gallons (0.189 m^3) of the reaction mixture containing oil was stripped in a 100 gallon (0.379 m^3) glass kettle at 300°F (148.9°C) and 20 mm Hg for 1 hour. Then it was transferred to a 50 gallon (0.189 m^3) stainless kettle and stripped at 400°F (204.4°C) and 20 mm Hg for 1 hour.

The final product had the following properties:

Viscosity at 100°C (15% polymer product by weight) = 2111 cSt

Viscosity of 2.8% solution in 100 N oil = 19.8 cSt

(Thickening Power).

The above-mentioned product was line mixed with a 3.75% solution of ethylene diamine (EDA) in C_{7-9} aromatic hydrocarbon solvent mixture. The polymer solution was pumped at 133.5 ml/min. and the EDA solution was pumped at 33.4 ml/min. The total mixture was then fed into a wiped film evaporator kept at 450°F (232.2°C). The stripped product was filtered through a 100 μ filter and had the following properties:

Flash Point = 300°F (148.9°C)

Viscosity at 100°C (15% by weight product) = 2558 cSt

Viscosity of 2.8% solution in 100 N oil = 20.5 cSt (at 100°C)

Nitrogen content = 98 ppm.

Multi-grade lubricating oils with good dispersancy and shear stability were prepared using the foregoing product of this Example.

Example 4

Eighty grams of the ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 was dissolved in 920 g of chlorobenzene at 110°C with stirring. The solution was cooled to about 25°C after which a mixture of cumene hydroperoxide and dicumyl peroxide, in the mole ratios shown in Table I below, were added thereto with mixing. The reaction mixture was pumped at 19.7 g/min into a 50 ml reactor tube (a one quarter inch (6.35 mm) stainless steel tubular reactor) which was maintained at 180°C and 200 psig (14.06 kg/cm^2). The residence time in the reactor was 2.75 minutes.

To 500 g of the reacted mixture were added 267 g of 100 Neutral oil. The chlorobenzene was removed from this mixture by distillation at 200°C and 20 mm Hg pressure yielding a 15% by weight solution of the oxidized polymer in oil.

A portion of the final product solution was then diluted to 2.8% by weight polymer using additinal 100

Neutral oil. The viscosity of the resulting 2.8% solution at 100°C in centistokes is what is defined as Thickening Power (TP).

The data in Table I demonstrates the effect of varying the mole ratio of peroxide to hydroperoxide on the thickening power of the oxidized polymer.

TABLE I

Run No.	Moles Dicumyl Peroxide	Moles Cumene Hydroperoxide	Mole Ratio of Peroxide to Hydroperoxide	TP*
1	0.33	0.07	4.7:1	44
2	0.30	0.13	2.3:1	28
3	0.27	0.18	1.5:1	20
4	0.22	0.26	0.8:1	21
5	0.19	0.33	0.6:1	27
6	0.15	0.40	0.4:1	32
7	0.11	0.46	0.2:1	37
8	0.07	0.53	0.1:1	58

*TP for starting polymer before oxidation was about 45 cSt

Example 5

To 4000 grams of a chlorobenzene solution containing 8% by weight of the ethylene/propylene/1,4-hexadiene terpolymer used in Example 1 were added 12.7 grams of cumene hydroperoxide and 29.7 grams of dicumyl peroxide with mixing. The reaction mixture was pumped at 33 g/min. into a 50 ml reactor tube (a one quarter inch (6.35 mm) stainless steel tubular reactor) which was maintained at 200°C and 200 psig (14.06 kg/cm^2). The residence time in the reactor was 1.5 minutes.

To 500 grams of the reacted mixture were added 118.13 g of 100 Neutral oil. The chlorobenzene was removed from this mixture by distillation at 200°C and 20 mm Hg pressure.

A portion of the final product solution was then diluted to 2.8% by weight polymer using additional 100

Neutral oil. The viscosity (Thickening Power) of the resulting 2.8% solution at 100°C was 12.7 cSt. The oxygen content of the product as determined by Neutron Activation Analysis was 0.33%. The acid content was 2.8 mmole COOH/100 g polymer and the hydroxyl content was 0.069 mmoles OH/100 g polymer.

Multi-grade lubricating oils with good dispersancy and shear stability were prepared using the product of this Example.

Example 6

Lubricating oil compositions in accordance with this invention was evaluated in the standard Sequence V-D automotive engine test. In the Sequence V-D test, lubricants containing the experimental additives are charged respectively to a standard internal combustion engine. The engine is operated at an assigned load and temperature, and at the end of a prescribed time the engines are disassembled and examined for deposits and wear. This engine test is a standard method well known in the industry.

Also, viscosity measurements at 100°C, 40°C and 0°C show acceptable viscosity measurements and with the use of pour point depressants, acceptable viscosity measurements at -32°C are obtained.

A. Standard Sequence V-D Engine Test

Formulated 10W-30 oils (Exxon 150 neutral) containing the viscosity index improvement additives shown in Table I were prepared and tested in a Sequence V-D Test method phase 9-2 (according to candidate test for ASTM) as shown in Table II below. This procedure utilizes a Ford 2.3-litre four-cylinder engine. The test method simulates a type of severe field test service characterized by a combination of low speed, low temperature "stop and go" city driving and moderate motorway operation. The effectiveness of the additives in the oil is measured in terms of the protection provided against deposits and valve train wear. Each of

the formulated 10W-30 oils also contained 3.5% of a polyisobutenyl succinimide (50% by weight concentrate in oil), 20 mmoles/kg overbased calcium sulfonate, 30 mmoles overbased magnesium sulfonate, 18 mmoles dialkyl dithiophosphate, 0.3% dialkyl diphenylamine and 1% of a sulfonate-succinimide reaction product overbased with potassium triborate.

TABLE II

Sequence V-D Performance

Average Formulation	Piston Sludge	Average Varnish	Cam Lab Varnish v. 10^{-3}	Wear inch Avg.	Max.
1.1% Product of Example 1	9.5	8.0	8.4	0.4	0.6
1.1% Product of Example 2	9.1	7.9	8.0	0.5	0.7
1% Product of Example 3	8.6	7.8	7.7	0.5	0.8
0.7% AMOCO 6565[1]	9.4	8.1	7.3	0.6	0.7
0.7% TLA 555[2]	9.1	7.7	8.0	0.5	0.7

[1] Commercial VI Improver - vinyl pyrrolidone grafted on to an ethylene/propylene copolymer.

[2] Commercial VI Improver - oxidized ethylene/propylene copolymer reacted with formaldehyde and an amine.

CLAIMS:

1. A method of oxidatively degrading an olefinic polymer, which comprises oxidizing the olefinic polymer in an inert solvent in the absence of molecular oxygen and in the presence of an oxidant mixture of at least one peroxide and at least one hydroperoxide, said oxidant mixture being present in an amount sufficient to effect molecular weight degradation and the mole ratio of peroxide to hydroperoxide being in the range from 3.2 to 1 to 0.4 to 1, whereby an oxidised polymer product is obtained.

2. A method according to Claim 1, wherein the olefinic polymer is a copolymer of ethylene and a C_3-C_8 alpha-olefin.

3. A method according to Claim 2, wherein the olefinic polymer is an ethylene-propylene copolymer.

4. A method according to Claim 1, wherein the olefinic polymer is a terpolymer of ethylene, a C_3-C_8 alpha-olefin and a non-conjugated acyclic or alicyclic diolefin.

5. A method according to Claim 4, wherein the olefinic polymer is a terpolymer of ethylene, propylene and 1,4-hexadiene.

6. A method according to any preceding claim, whrein the oxidizing reaction is carried out at a temperature in the range from 60 to 250^{o}C and under a pressure of from 0 to 1,000 psig (1 to 70.3 kg/cm^2).

7. A method according to any preceding claim, wherein the oxidant mixture is present in an amount of from 1 to 20% by weight, based on the olefinic polymer.

8. A method according to any preceding claim, wherein the hydroperoxide in said oxidant mixture is hydrogen peroxide, cumene hydroperoxide, tertiary butyl hydroperoxide, or 2,5-dihydroperoxy-2,5-dimethylhexane, and the peroxide in said oxidant mixture is dicumyl peroxide, benzoyl peroxide, or dilauryl peroxide.

9. A method according to Claim 8, wherein the oxidant mixture comprises hydrogen peroxide and dicumyl peroxide.

10. A method according to Claim 8, wherein the oxidant mixture comprises cumene hydroperoxide and dicumyl peroxide.

11. A method according to any preceding clim and further comprising reacting the oxidised polymer product with an organic amine containing at least one primary or secondary amino group.

12. A method according to Claim 11, wherein the organic amine is a polyalkylene polyamine having the general formula:

$$H_2N(CH_2CHR^1NH)_xH$$

wherein each R^1 is hydrogen or a C_1 to C_6 alkyl group and x is an integer in the range of from 1 to 10.

13. A method according to Claim 12, wherein the amine is ethylene diamine.

14. An oxidised polymer product obtained by the method claimed in any preceding claim.

15. A lubricating oil composition comprising an oil of lubricating viscosity and, as a viscosity index improvement agent, an oxidised polymer product as claimed in Claim 14.